



The Transformation of Black Carbon Aerosols from Hydrophobic to Hydrophilic and the Impact on its Global Distribution



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Abstract

Most models apply a fixed transformation time of black carbon (BC) aerosols from hydrophobic to hydrophilic. Here a more physically-based parameterization scheme is developed. Three mechanisms are studied, which are the condensation by H₂SO₄ vapor and coagulation by H₂SO₄ nuclei, the coagulation with pre-existing water-soluble aerosols, and the interstitial scavenging in clouds. It is found that the transformation is more than 10 times faster in polluted than in remote areas. The Condensation of H₂SO₄ vapor ranges from the most important to the least important mechanism among the three, depending on the supersaturation of the precipitating clouds. The coagulation of hydrophobic BC aerosols with pre-existing water-soluble aerosols is important only in polluted areas, while the coagulation with cloud droplets is relatively more important in remote areas.

A global chemistry model, MOZART II, is applied to assess the impact of a parameterized transformation time on BC aerosol distribution. The results are compared with simulations using a global uniform transformation time (control run). It is found that by setting the cloud supersaturation at 0.8%, BC aerosol concentration is reduced in polluted areas, and is increased in biomass burning and remote areas by using a parameterized transformation time (parameterized run). The increase is especially prominent in South Africa and South America (the major biomass burning areas), Antarctica, and higher atmospheric altitudes. The case by setting the cloud supersaturation at 0.1% produces a weaker reduction, and a much stronger increase, when compared with the control run. A preliminary comparison of the control run with observations indicates that the variable transformation rate in the parameterized run (the supersaturation of 0.8% case) improves the agreement between model and observations.

Model Description

A box model was set up for the study of the role of H₂SO₄ vapor. The model has four species: H₂SO₄ vapor, sulfate nuclei, hydrophobic BC aerosols, and pre-existing accumulation mode aerosols. Aerosol microphysical processes included are:

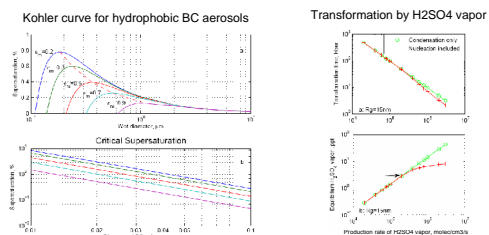
- nucleation and condensation of H₂SO₄ vapor
- self-coagulation of sulfate nuclei
- coagulation of sulfate nuclei on hydrophobic BC aerosols and other aerosols

The production rate of H₂SO₄ vapor by SO₂ oxidation with OH is the input of the model. The coagulation with pre-existing water-soluble aerosols and cloud droplets are also studied. A parameterization scheme of the transformation time is developed and applied to a 3D global photochemistry model MOZART II.

The chemical mechanism in MOZART II used for this study includes oxidation schemes for nonmethane hydrocarbons (NMHCs) and heterogeneous reactions of NO₂ and NO₃ on sulfate aerosols. Totally 73 species are simulated, and 178 reactions are included. Surface emissions include those from fossil fuel burning and other industrial activity, biomass burning, biogenic emissions from vegetation and soils, and oceanic emissions. Meteorological parameters are archived from an MACCM3 run and are provided to MOZART every 3 hours. The transport processes include advection, deep and shallow convections, and vertical diffusion. Dry deposition and wet scavenging are included in the model as deposition velocities and first-order loss process respectively.

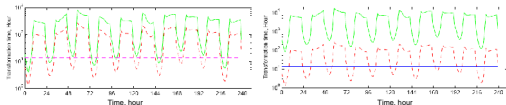
The Transformation from Hydrophobic to Hydrophilic

(1) The role of H₂SO₄ vapor



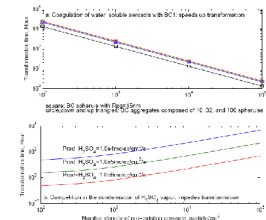
(left, top) Kohler curve for hydrophobic BC aerosols coated by sulfate with different thickness. The diameter of BC core is assumed to be 50nm, the critical supersaturation is indicated by the red dash line.
(left, above) The critical supersaturation for hydrophobic BC aerosols with different size and sulfate coating.
(right, top) The variation of transformation time with the production rate of H₂SO₄ vapor, with and without homogeneous nucleation. Greater H₂SO₄ vapor production rate leads to faster transformation, and nucleation speeds up the transformation.
(right, above) The corresponding equilibrium H₂SO₄ vapor pressure. The critical H₂SO₄ vapor above which homogeneous nucleation has an effect is indicated by the arrow. Nucleation keeps the H₂SO₄ vapor pressure at a low level.

Different Transformation time with different BC size and supersaturation



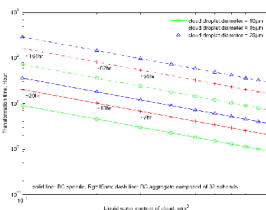
The transformation time diagnosed in MOZART II. The case represents an polluted area in China in January 11-20. (left) Large BC aerosol (red dash) has a faster transformation (T11) by condensation of H₂SO₄ vapor than small one (green solid), since less water-soluble coating mass is required to convert it from hydrophobic to hydrophilic. (right) For the same reason, (red dash) higher supersaturation produces a faster T11. The transformation by coagulation with pre-existing water-soluble aerosols changes with size mildly (left, blue solid and purple dash), and does not depend on the supersaturation (right, blue solid).

(2) The role of pre-existing aerosols



Pre-existing water-soluble aerosols speed up the transformation by coagulating with BC aerosols (T12), and slow down the transformation by competing with BC aerosols in the condensation of H₂SO₄ vapor.

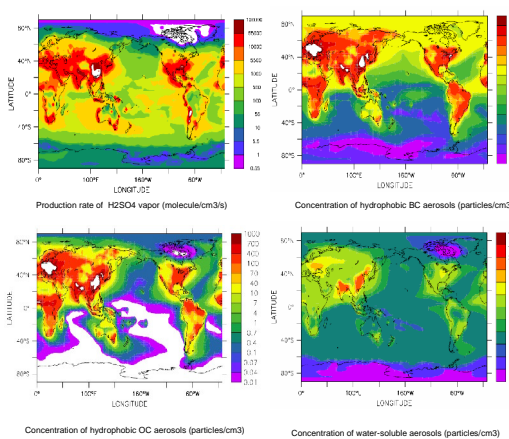
(3) Interstitial scavenging in clouds



The transformation by interstitial scavenging (T13) varies inversely with liquid water content (LWC) of clouds for a fixed cloud droplet size. Larger cloud droplets produce a slower transformation. BC aggregates have a slower transformation compared to BC spherules due to its larger size that is closer to the size of cloud droplets.

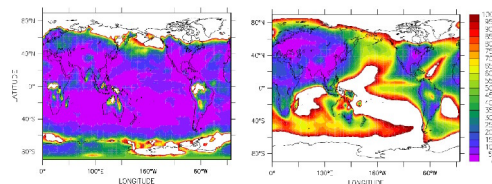
The Transformation Time

(1) The driving forces in the transformation

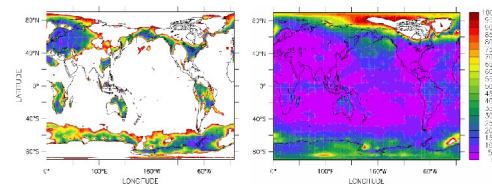


The production rate of H₂SO₄ vapor is the primary driving force in the transformation by condensation of H₂SO₄ vapor. The large amount of hydrophobic OC aerosols and water-soluble aerosols (including components of SO₄, NH₄, NH₄NO₃, hydrophilic BC and hydrophilic OC) compete with hydrophobic BC aerosols in the process.

(2) The global distribution of transformation time

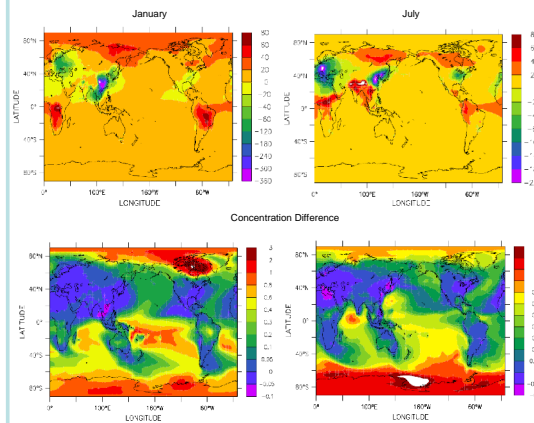


The global distribution of transformation time in January in the surface layer. (left) T11 (hr): by H₂SO₄ vapor condensation. Supersaturation (Sc) is assumed to be 0.8%, which requires a sulfate coating of 19% of aerosol mass for BC aerosol to be activated. If Sc is assumed to be 0.1%, a sulfate coating of 94% of aerosol mass is needed to activate the BC aerosol, and a much larger T11 is resulted than shown above, and the importance of mechanism 1 is also reduced tremendously. (right) T12 (hr): by coagulation with water-soluble aerosols.



The global distribution of transformation time in January in the surface layer. (left) T13 (hr): by interstitial scavenging in clouds. (right) Tt (hr): the overall transformation time by including all the three mechanisms.

The Difference in BC Aerosol Concentration with Control Run



The difference in BC aerosol concentration (ppt) with control run in the surface layer. BC aerosol concentrations decrease over polluted source regions in northern mid-latitudes, and increase in biomass burning and remote regions. The mass fraction of sulfate coating is 19%. Interstitial scavenging in clouds is not included.

Conclusions

• Condensation of H₂SO₄ vapor is found to be the most important mechanism in the transformation process by assuming a high limit supersaturation. The typical transformation time for this mechanism ranges from about 10 hours to 50 hours in urban and urban-influenced rural areas, and the transformation time in remote areas is on the order of 100 hours or even longer. The importance of this mechanism is reduced tremendously by assuming a low supersaturation. As a comparison, most models assumed a global uniform transformation time in the range of 24 to 48 hours.

• When the transformation by interstitial scavenging in clouds is included in the global model, the reduction is strengthened and the increase is weakened, because a faster transformation produces a lighter atmospheric load. However, polluted areas in northern hemisphere are affected less than remote areas and high levels, due to the relative importance of clouds in the transformation processes.

• The global modeling of BC aerosol distribution in MOZART II shows a reduction in most polluted areas in northern hemisphere, and an increase elsewhere especially in the biomass burning regions and the polar areas.

Discussions

• Other mechanisms such as the oxidation of organic carbon on the surface of BC aerosols and the ice nucleation of BC aerosols will speed up the transformation process.

• Preliminary comparison with observations indicates that the bias of control run, such as the low bias in biomass burning and remote areas and high bias in polluted areas could be lowered by applying the physically-based parameterization scheme for the transformation time.

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